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DIPHENYLCHLOROBORON SALTS (Ph₂B(OH)₂)

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The heterolytic decomposition (disproportionation) of phenylboron chloroformate in the chlorobenzene medium yields a cation of diphenylchloroboron as a result of transfer of the phenyl cation to the unshared pair of electrons of chlorine. The reaction as to its character and the end result is almost completely similar to the one described by the authors¹ for the synthesis of diphenyl boron phenoxide cations. During a disproportionation reaction in which successive amounts of phenylboron chloroformate are added (48 g. total quantity) within a period of 1-1/2 hours to 100 ml. of chlorobenzene heated to about 60° C. and the mixture being mixed during this addition in a flask fitted with a reflux condenser, the phenyl chloroboron salt may be isolated by water extraction (2 successive portions 30 ml. quantities of water).

The aliquot portions of the above extract were treated with various amounts. On treatment with potassium iodide the preliminary precipitate of tetrabenzylboron iodide is transformed into a liquid mixture of chlorobenzene and benzene. This testifies to a considerably lesser stability of chloroboron salts (as compared to those prepared by these authors) compared to the diphenyl chloroboron salt synthesized in 1952 by Austin and May².

From 10 ml. of the above mentioned water extraction the authors have carried out precipitation with a strong solution of tetraphenylboron sodium to obtain a tetrabenzylboron salt of diphenyl chloroboron. Reprecipitation by the same method from an acetone solution followed by two further precipitations gave a yield of the pure salt which was found to decompose at 160-161° C. Found, upon the completion of the above mentioned purification of the product, shiny, plate crystals, quite soluble in acetone and benzene, but completely insoluble in cold water or in ether.

Found %: C 35.75, 35.02; H 6.17, 6.05; in CHCl₃, 4.0%; in benzene, 3.5%
Calc. for C₂₀H₁₆Cl₂B: C 34.95; H 5.95; Cl 6.99; B 1.4%

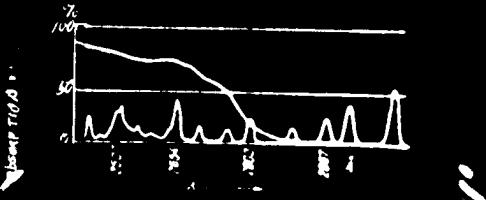


Fig. 1. Absorption Spectrum of Tetraphenylboron Diphenyl Chloroboron Salt.
Solvent Methanol. Molecular Concentration 3×10^{-4} . λ_{max} 2951 Å ($\nu_{max} 3.41 \text{ cm}^{-1}$).
The Reference spectrum of mercury is shown with the above chart.

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The absorption spectrum of tetraphenylboron-diphenyl chloronium salt is shown in Fig. 1, while the comparable spectrum of tetraphenylboron potassium is shown in Fig. 2. This latter spectrum was obtained under exactly similar conditions using methanol as a solvent.

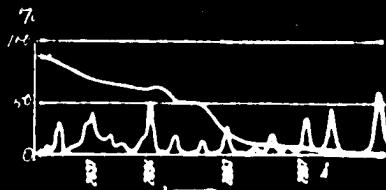


Fig. 2. Absorption spectrum of tetraphenylboron potassium. (Infrared spectrum. Molar concentration 3×10^{-4} ; λ_{max} mcs 1 (ν_{max} 3,300 cm^{-1}); ν_{min} 1,600 cm^{-1}).

Twenty ml. of the second water extraction 0.07 g. of diphenyl chloronium iodide and phenoxide are precipitated with the addition of a concentrated solution of silver nitrate and in 10% HCl. After recrystallization from nitroethane, the decomposition point of the diphenyl chloronium chloroplatinate salt was found to be 140-145 $^{\circ}\text{C}$. These small light-yellow crystals were found to be decomposed in water and in alcohol, considerably more soluble in hot NMP, soluble in nitroethane, and insoluble in ether. This salt was found to be stable upon heating in the laboratory.

Found %: C 36.54, 36.73; H 2.39, 2.47; P 15.14, 15.48
Calc. for $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{P}_2\text{I}_2$ %: C 36.60; H 2.37; P 15.71

Upon addition of 17 ml. of the second water extraction to the solution of phenoxide in aqueous sodium iodide, 0.45 g. of diphenyl chloronium potassium double complex salts were precipitated. After two reprecipitations from nitroethane with acetone-ether, the decomposition point of the resultant purified salt was found to be 100-100.5 $^{\circ}\text{C}$. These light-yellow crystals were found stable after keeping them in the laboratory for several weeks. They were found to be soluble in acetone and in nitroethane, insoluble in water and in ether.

Found %: C 19.04, 18.75; H 1.34, 1.25
Calc. for $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{K}_2\text{I}_2$ %: C 18.69; H 1.31;

The relatively small yields of diphenyl chloronium cations are not surprising since under the conditions of decomposition of phenyl diisodium fluorobenzene the conditions for formation of diphenyl chloronium salts are not too favorable. The resulting reaction product was found to be (under conditions described in the above synthesis tests) fluorobenzene as obtained by the Schiemann reaction. It is evident that to obtain decent yields of diphenyl chloronium cation it is necessary to create such conditions that its salt would be withdrawn from the reaction mixture as soon as it is formed.

The above described tests as well as those tests described in our previous article¹ reveal a method of preparation of simple aromatic members of a new class of diaryl-bromonium and diaryl chloronium salts which offers relatively simple synthesis of these interesting compounds.

¹ Bezymyanov, A.N. and Tolstaya, T.P., DAS 104, (6) 1975. ² Smidin, R.B. and Bay, A.S., J. Am. Chem. Soc., 74, 274 (1952). Translated by V.V. Levashoff, 7/11/78